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**Relationships Among Benthic Macroalgal Biomass, Sediment Dissolved Sulfides, and Infaunal Invertebrates in Yaquina Estuary, Oregon**

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**ABSTRACT**

Benthic surveys were conducted between June 2000 and February 2001 along two intertidal band transects off Idaho Pt. and Coquille Pt. within Yaquina estuary, Oregon, USA. Samples were collected at random positions along 16 line stations between the upper margin of the native eelgrass (*Zostera marina*) meadow near the estuary channel and the upper intertidal zone. Surficial sediment cores were taken for geochemical analyses and quantification of infaunal amphipods, and the biomass of accumulated benthic macroalgae (principally *Ulva*) was determined. Very large reductions in amphipod numbers were measured in a major sector of the Idaho Pt. transect, relative to corresponding measurements off the Coquille Pt. reference site. Distinct effects on benthic shrimp and bivalve mollusks also were observed. Sediment pore water samples revealed 100-fold increases in dissolved sulfides beginning in September and extending through November, relative to earlier collections along this transect and to typical levels measured along the Coquille Pt. transect. Survey median concentrations of the most toxic component of dissolved sulfides, un-ionized H<sub>2</sub>S, calculated for the Idaho Pt. pore water samples collected in this three month period were four to eight times the median LC<sub>50</sub> for H<sub>2</sub>S (5.5 µM) determined from reported sulfide toxicity studies on benthic/epibenthic marine crustaceans and bivalve mollusks. These levels appear to be high enough to account for the altered distributions

of invertebrates observed along the Idaho Pt. transect. Both elevated accumulations of benthic macroalgae and higher proportions of fine-grained sediments there may contribute to the high concentrations of dissolved sulfides measured at this site.

## INTRODUCTION

### Benthic Macroalgae

As human populations and activities increase in coastal zones around the world, there is increasing concern regarding the resultant eutrophication of estuarine and nearshore marine ecosystems (Short and Wyllie-Echeverria, 1996; Hemminga and Duarte, 2000; Orth et al., 2006). One aspect of such eutrophication is the occurrence of intertidal benthic macroalgae in densities sufficient to cause offensive odors and/or impact epibenthic and benthic communities. For example, Nicholls et al. (1981) reported a decrease in estuarine infauna populations with an average macroalgal cover density of about 40% on the southern coast of England. Working in the same region, Tubbs and Tubbs (1983) found that a cover density exceeding 25 % in 40% of the intertidal area corresponded to a reduced abundance of zoobenthos. Hull (1987) reported a decrease in amphipod abundance on the east coast of Scotland with a macroalgal biomass as low as 60 grams dry weight per square meter (gdw/m<sup>2</sup>). Further work in that area by Raffaelli et al. (1991) showed a 90% decrease in amphipod abundance with macroalgal densities of about 200 gdw/m<sup>2</sup>. On the north Baltic Sea, Norkko and Bonsdorf (1996a) reported a 90% decrease in benthic organisms when macroalgal densities there reached 440 gdw/m<sup>2</sup>. Norkko (1998) also reported a decrease in juvenile bivalve mollusks in the region with an average macroalgal cover of 50%. Further work there by Norkko et al. (2000) demonstrated a reduction in both bivalve and amphipod densities when macroalgal abundance reached 180 gdw/m<sup>2</sup>. On the west coast of

Sweden, Osterling and Pihl (2001) found a 90% decrease in suspension-feeding bivalves with a macroalgal density of 300 gdw/m<sup>2</sup>. Lewis et al. (2003) reported a decrease in amphipod abundance on the south coast of Ireland when macroalgal densities exceeded 200 gdw/m<sup>2</sup>. On the east coast of Australia, Cummins et al. (2004) found decreased abundances of polychaetes and mollusks with a macroalgal density of 450 gdw/m<sup>2</sup>. Finally, Jones and Pinn (2006) reported a 70% decrease in infaunal abundance and biomass when macroalgal cover reached 90% on the southern coast of England.

### **Dissolved Sulfides Toxicity**

Most of these studies also reported either the co-occurrence of hydrogen sulfide or low Eh values representative of reducing conditions in the target estuarine sediments. Numerous investigations have shown that dissolved sulfides are toxic to marine invertebrates. In an early study, Caldwell (1975) reported results of laboratory tests on the amphipods *Anisogammarus* and *Corophium*, the isopod *Gnorimosphaeroma*, and zoeae of the *Cancer* crab that yielded 96-hour LC<sub>50</sub> values (concentrations causing 50% mortality) for dissolved sulfides (pH 7.9-8.7) with a median value of 22 micromoles per liter (μM). He also reported 96 hour LC<sub>50</sub> values of 16 and 31 μM (pH = 8.0-8.2) for the zoea and first instar stages of the crab *Cancer*, respectively, and values of 44 μM for the oyster *Crassostrea* (pH 7.9-8.7) and 187 μM for the clam *Balthica* (pH 7.8-8.6). Knezovich et al. (1996) measured 48-hour LC<sub>50</sub> values of 50 and 104 μM from dissolved sulfides test (pH = 7.8-8.2) on the amphipods *Rhepoxynius* and *Eohaustorius*, respectively. Similar findings were obtained by Gopakumar and Kuttyamma (1996), who reported median 96 hr LC<sub>50</sub> values for un-ionized H<sub>2</sub>S exposed to the marine shrimp *Penaeus* and *Metapenaeus* (size range 35-40 mm) that correspond to approximately 300 and 360 μM dissolved sulfides (pH 8.1-8.3), respectively. Finally, Laudien et al. (2002) observed that, after

two hours of exposure to 100  $\mu$ M dissolved sulfides in test sediment, juvenile surf clams (*Donax*) moved to the sediment surface.

It should be noted that the variable “dissolved sulfides” is comprised of two major chemical species, un-ionized  $H_2S$  and the bisulfide ion  $HS^-$ , whose proportions are dependent mainly upon the pH of the solution, but also upon salinity and temperature. The  $H_2S$  component generally is considered to constitute most of the toxicity of the dissolved sulfides variable (Hagerman and Vismann, 1995), because this un-ionized molecule can diffuse across an organism’s membranes and block aerobic metabolism by inhibiting cytochrome c oxidase (Theede, 1973; Sandberg-Kilpi et al., 1999). At a pH of 8.0 (and salinity 30 parts-per-thousand, ppt; temperature 15 degrees Celcius, deg C), less than 10 % of the dissolved sulfides occurs as  $H_2S$ . However, at a pH of 7.5 approximately 20 % occurs as  $H_2S$ , and at a pH of 7.0 almost 45 % occurs as  $H_2S$  (Standard Methods, 1995). Thus, pH values generally are reported along with dissolved sulfides toxicity values to permit calculation of the most toxic component,  $H_2S$  (Wang and Chapman, 1999).

## BACKGROUND AND OBJECTIVES

The study described here was conducted in response to relatively high levels of benthic macroalgal cover and biomass observed in Yaquina estuary on the central Oregon coast, USA (Figure 1). Aerial photographic surveys conducted in the summer of 1997 and 1998, accompanied by detailed ground surveys, revealed extensive distributions of benthic green macroalgae on the intertidal mudflats upslope of the native eelgrass (*Zostera marina*) beds (Young et al., 1999). Therefore, during the summer of 1999 Young conducted a systematic survey of eelgrass and benthic macroalgal cover and biomass at six intertidal sites situated

approximately evenly along the range of *Z. marina* in lower Yaquina estuary (Young et al., 2003). The results indicated that the site off Idaho Pt. had distinctly higher accumulations of benthic macroalgae, and frequencies of H<sub>2</sub>S odor detection, than did the site off Coquille Pt. across the main channel, or at the other four survey sites. Thus, the study reported here was initiated at the Idaho Pt. and Coquille Pt. sites in June 2000, with three major objectives. The first objective was to quantify the spatial-temporal distribution of dissolved sulfides in pore water of surficial sediment (0-5 cm) from the Idaho Pt. and Coquille Pt. sites. The second was to examine whether there was any evidence of an impact on infaunal invertebrates at the Idaho Pt. site, and whether the levels of dissolved sulfides there were high enough to explain any impacts observed. The third objective was to seek differences in conditions at the two sites that might have contributed to corresponding differences in dissolved sulfide concentrations.

## APPROACH

### Sampling

At the two study sites (Figure 2) band transects 30 m in width were established, beginning 25-35 m downslope of the upper boundary of the native eelgrass meadow and extending almost to the upper edge of the intertidal zone. Station lines parallel to the channel were established every 10 m for the first 100 m, with the lowest three lines off Idaho Pt. (labeled A–C) situated within the eelgrass meadow, and the lowest four lines (A–D) situated within the eelgrass meadow off Coquille Pt. Beyond 100 m the separation between station lines (of approximately constant elevation) increased to 45 m off Idaho Pt. and 40 m off Coquille Pt., terminating at line station P approximately 40 m downslope of the rockweed (*Fucus*) boundary

of the upper intertidal zone. (Limited sediment measurements also were made near this boundary at Station Q).

During 2000, surveys were conducted at low tide every other week during summer and early fall, and then approximately every month through December. One midwinter survey was conducted in early 2001. In each low tide survey, at specified line stations three randomly selected distances between 1 m and 30 m first were obtained. Then, starting at the 0 m mark of a given line, the surveyor walked the randomly determined distance into the band transect and placed a quadrangle (0.5 m on a side, strung with two orthogonal sets of five equally-spaced taut lines) 1 m upslope or downslope of the transit path (in alternating low-tide surveys). Percent cover values of eelgrass (*Z. marina* or *Z. japonica*) and benthic green macroalgae (*Ulva* spp.) were measured using the point-intercept method or estimated visually. Then, again randomizing, at two of the three line stations a vegetation biomass sample was collected from the lower left 0.25 m x 0.25 m portion of the quadrangle. Next, a sediment core (15-cm internal diameter) and two adjacent cores (8-cm internal diameter) were collected at one of the three stations, again randomizing; these were capped for subsequent geochemical and benthic infaunal analysis, respectively. The cores were returned to the laboratory and refrigerated within three hours of collection. Sediment temperature was recorded at each core station by inserting a glass thermometer ( $\pm 0.2$  deg C) to a depth of 5 cm. Density classes of benthic shrimp holes (*Upogebia* spp. and *Neotrypaea* spp.), and presence/absence indices of bivalve mollusk shells within the 0.5 m x 0.5 m quadrat, also were determined. In December 2001, an additional sediment core was taken from the native eelgrass bed within the Idaho Pt. transect, using a 30 cm long barrel containing ports spaced every 3 cm. Upon withdrawal from the immersed sediment, the bottom and top of the barrel was capped and taped, the ports were taped, and the core was

maintained in a vertical position and returned to the laboratory where pH measurements were made within two hours (below).

### **Analyses**

The top 5 cm of the geochemical core was extruded in a vertical position under a N<sub>2</sub>-filled glove bag, and 250 ml centrifuge tubes were packed with this sediment and tightly capped within this oxygen-free environment. The samples then were removed from the bag, paired by mass and centrifuged at 4500 rpm (3300 g) for 20 minutes. Next, the tubes were transferred to a N<sub>2</sub>-filled glove bag and sequentially opened for processing. A water sample then was withdrawn into a plastic syringe, a 0.45-μ Cameo filter was inserted onto the tip, and the sample was expressed through the filter into a clean glass beaker. Given sufficient volume, duplicate 5.0 ml samples of the filtered pore water were withdrawn using an Eppendorf pipet and 20 μL of 2 N zinc acetate was added and homogenized to precipitate and preserve the dissolved sulfide sample. If the volume of pore water was limited, a single sample of known volume was taken and preserved. Duplicate 0.5 ml and 0.05 ml aliquots also were withdrawn and preserved for possible analysis of high-concentration samples (if necessary, final samples also were diluted with de-oxygenated deionized water so that their signal values fell within the linear range of the calibration curves ). The samples were analyzed for total dissolved sulfides ( $\sum S^-$ ) utilizing the methylene blue colorimetric method and a Shimadzu UV-2101PC spectrophotometer (Method 4500-S<sup>2-</sup>, Standard Methods, 1995). Calibration curves were based upon absorbance signals from six  $\sum S^-$  standards prepared in de-oxygenated distilled water, with concentrations ranging from about 0.15 to 1.5 mg sulfur per liter. A separate pore water sample was collected and analyzed for pH (using an Orion 250A meter calibrated with 7.00 and 10.00 pH buffer solution), and for salinity (using a temperature-compensated American Optical - Reichert refractometer

whose factory calibration was confirmed using Standard Sea Water, Inst. of Oceanographic Services, Surrey, England). As described above, a program to check the pH values obtained in the supernatant of centrifuged surficial sediment samples was initiated in December 2001.

Within two hours of collection, *in situ* pH measurements were obtained along the length of the special pH core by inserting the probe of a calibrated pH meter directly into sediment through the uncovered ports. Meter readings also were obtained in certified pH buffer solution at the beginning and the end of these core profile measurements, and corrections made to the individual values assuming linear drift of meter readings with time. For the surveys conducted in 2000, a 100 ml aliquot of the centrifuged sediment sample was taken for subsequent analysis of total organic carbon (TOC) by combustion after acidification (Tetra Tech, 1986), and particle size distribution using sequential sieving (Buchanan, 1984). In addition, upon return to the laboratory the benthic macroalgal samples were washed free of sediment in tap water, sorted to obtain green macroalgal samples, and dried to constant weight at 70 deg C.

### **Amphipod Identification**

The infaunal core samples were combined and sieved through a 1.0 mm screen. The organisms retained were preserved in buffered 10% formalin and stained with Rose Bengal. The samples then were transferred to 70% ethanol and sorted under magnification. The amphipod species were identified to species and counted following guidance provided by Dr. John Chapman (personal communication), and described recently in the Light and Smith manual on intertidal invertebrates (Chapman, 2007).

## **RESULTS**

### **Infaunal Amphipod Abundance**

Thirteen infaunal amphipod species were identified in the surficial sediment samples collected along the Coquille Pt. transect between June and December, 2000 (seven low tide surveys); the corresponding number for the Idaho Pt. transect was ten species (ten low-tide surveys). The total number of individuals of each species counted in each transect's samples during this interval is listed in Table 1. Total numbers of amphipods counted in the sediment samples from a given station and survey date for the Coquille Pt. and Idaho Pt. transects are listed in Tables 2 and 3, respectively, and the average station density (per 100 cm<sup>2</sup> of sediment surface) for June – December 2000 is shown in Figure 3. Median abundance classes for benthic shrimp burrows observed within the core quadrats are listed in Table 4, and presence or absence indices for bivalve mollusk shells observed in the quadrats are listed in Table 5.

### **Sediment Geochemistry**

Average concentrations of  $\Sigma S^-$  obtained from the replicate aliquots of surficial sediment pore water for these transect stations and dates are listed in Tables 6 and 7, respectively. Median pore water pH, salinity, and surficial sediment temperature values obtained for a given survey at the Idaho Pt. site are listed in Table 8.

Percent dry weight concentrations of TOC measured in surficial sediment samples collected from the transect stations during June, July, September and October/November 2000 are shown in Figure 4. Values for percent fines (grain diameter < 0.063 mm) in surficial sediment samples collected from the Coquille Pt. and Idaho Pt. band transects in July 2000 are shown in Figure 5.

### **Benthic Macroalgae**

On the basis of these results, three bathymetric zones were established to compare and evaluate the data. For each transect, Zone I included the three station lines nearest the upper

boundary of the eelgrass meadow (Idaho Pt.: A-C; Coquille Pt.: B-D). Zone II included the next three lines upslope of this boundary (Idaho Pt.: D-F; Coquille Pt.: E-G). Zone III included lines H through O in each transect, where the greatest difference between total amphipod numbers at the two sites occurred (Figure 3). For a given survey, an average value for benthic green macroalgal biomass was obtained for each of these zones at the two sites (Figure 6). Typical numbers of samples collected from Zones I, II and III were 6, 6, and 16, respectively. Combination of the individual survey values for the growing season (June – November) for each zone yielded the summary statistics listed in Table 9.

## DISCUSSION AND CONCLUSION

The results presented in Tables 1–3 and Figure 3 indicate a clear difference in the distribution of infaunal amphipods between the two study sites during the survey period (June – December, 2000). The average number of amphipods counted per survey in the samples from the Coquille Pt. transect (1125 total / 7 surveys = 161 individual per survey) was almost four times that obtained for the Idaho Pt. samples (451 total / 10 surveys = 45 individuals per survey). However, most of this difference occurred within bathymetric zone III bounded by station lines H through O (Figure 3). This zone includes approximately 70% of the total area of the band transects surveyed during 2000. The median ratio for the densities of amphipods within Zone III at these two sites was 0.034 (range: 0.011 – 0.50), corresponding to a median reduction factor of 97% for total amphipod density at Idaho Pt. relative to the Coquille Pt. reference site. In contrast, the differences observed between abundance classes of benthic shrimp burrows at the two sites during July – September extended from station lines D through O (Table 4); thus, a second bathymetric zone (II) was defined as that zone encompassing the three station lines just

upslope of the eelgrass meadow upper boundary. Further, in September 2000 there was a distinct impact on near-surface infaunal bivalve mollusks along the Idaho Pt. transect, extending from line B within the eelgrass meadow to line P near the upper edge of the transects at the two sites (Table 5). Thus, for purposes of comparison the zone encompassing the three station lines just downslope of the eelgrass meadow upper boundary was defined as Zone I.

Very clear differences in characteristics of the surficial sediment collected from the two sites also were obtained. Relatively high concentrations of  $\Sigma S^-$  were measured in many of the supernatant pore water aliquots of the centrifuged sediment samples from the Idaho Pt. transect (Table 7), compared to those from the Coquille Pt. site (Table 6). Although the former values were highly variable, beginning with the mid-September collection a major increase in  $\Sigma S^-$  was observed. For example, the values obtained for the August 30 and September 14 collections from Station H were 13 and 1400  $\mu M$ , respectively; corresponding values for Station K were 2.1 and 200  $\mu M$ , and for Station O were 0.6 and 72  $\mu M$ . Thus, 100-fold step-function increases in  $\Sigma S^-$  concentrations were measured in some of the Zone III stations of the Idaho Pt. transect over a two week interval in early September. Such increases during this interval also were observed at other points along the transect. The  $\Sigma S^-$  concentration increased from 5.3 to 600  $\mu M$  at Station A, from 0.0 to 2300  $\mu M$  at Station C, and from 1.6 to 93  $\mu M$  at Station D. The period of highly elevated concentrations of pore water  $\Sigma S^-$  extended through the mid-November sampling, tapering off in December. The highest value measured in the samples collected on February 9, 2001 was 3.0  $\mu M$ . This condition along the Idaho Pt. transect was clearly different than that observed along the Coquille Pt. transect, where the highest value measured in 2000 was 8.1  $\mu M$ , and only two other values above 1  $\mu M$  were obtained. Application of the Welch two-sample t-test for non-equal variances showed that the difference in the mean  $\Sigma S^-$  values for September –

November at the two sites was highly significant ( $p < 0.001$ ). Thus, a major contrast between the two sites in Yaquina estuary was observed for both biological and chemical components of the intertidal ecosystem.

The next step taken in the evaluation was to calculate the corresponding concentrations of un-ionized  $\text{H}_2\text{S}$  from the station values of  $\Sigma\text{S}^-$ , in order to compare the levels of this most toxic component in our field samples to the corresponding  $\text{LC}_{50}$  values obtained from the dissolved sulfide toxicity test reports discussed above. For this purpose, we used the median values of pH, salinity and temperature obtained from each survey to calculate a corresponding ratio of  $\text{H}_2\text{S}$  to  $\Sigma\text{S}^-$  from the algorithm given in Standard Methods (1995). Of these three field variables, pH is by far most important in determining this ratio. As a check on our pore water pH values, we compared the median values we obtained for the Idaho Pt. transect between June and December 2000 to those obtained from the special pH core collected from Zone I of the Idaho Pt. transect on December 12, 2001. Our survey median values ranged from 7.08 to 7.24 with an overall median of 7.13 (Table 8), while values of 7.12, 7.15, and 7.06 were obtained at depths of 4, 7, and 10 cm, respectively, below the pH core's surface (Dr. Peter Eldridge, personal communication). Thus, the relatively low pH values we obtained from our June – December 2000 surveys are consistent with those obtained independently by Eldridge in December 2001. The ratios of  $\text{H}_2\text{S}$  to  $\Sigma\text{S}^-$  obtained for each of our Idaho Pt. transect surveys are listed in Table 8. These ratios may be applied to the individual station values of  $\Sigma\text{S}^-$  (Table 7) to obtain the corresponding values of un-ionized  $\text{H}_2\text{S}$  for the Idaho Pt. transect surveys.

To obtain comparable  $\text{LC}_{50}$  values for un-ionized  $\text{H}_2\text{S}$  from the published  $\text{LC}_{50}$  values for  $\Sigma\text{S}^-$ , we used the reported pH, salinity, and temperature values for each toxicity test to calculate the corresponding molar concentrations of un-ionized  $\text{H}_2\text{S}$  (using linear interpolation when

necessary). Combining the results we obtained from the data reported by Caldwell (1975), Gopakumar and Kuttyamma (1996), and Knezovich et al. (1996), the median calculated LC<sub>50</sub> value for seven infaunal or epibenthic marine crustaceans was 5.7  $\mu\text{M}$  H<sub>2</sub>S (range: 0.56 – 7.5  $\mu\text{M}$ ). The corresponding value for two bivalve marine mollusks was 5.4  $\mu\text{M}$  H<sub>2</sub>S (range: 3.4 – 7.5  $\mu\text{M}$ ). Based upon these values, 69% of the un-ionized H<sub>2</sub>S concentrations obtained for the Zone III pore water concentrations during September – November 2000 exceeded the median H<sub>2</sub>S LC<sub>50</sub> value for benthic crustaceans of 5.7  $\mu\text{M}$ . Similarly, for the two September surveys, 75% of the values for the entire Idaho Pt. transect exceeded the median H<sub>2</sub>S LC<sub>50</sub> value for marine bivalves of 5.4  $\mu\text{M}$ . This analysis provides an explanation for the relatively high abundance of bivalve mollusk shells observed during September on the sediment surface within the Idaho Pt. transect. For benthic shrimp, no  $\Sigma\text{S}^-$  toxicity values were located. Nevertheless, the relatively high frequency of  $\Sigma\text{S}^-$  levels along the Idaho Pt. transect might well have contributed to the lower burrow densities of this infaunal crustacean observed there between July and September, 2000. For the marine amphipods identified and quantified in this study, we note that these infaunal invertebrates nurture their young in broods (Dr. John Chapman, personal communication). Thus, the approximate three-month period (September – November) when toxic levels of dissolved sulfides predominated in surficial sediment off Idaho Pt. could have reduced the infaunal amphipod populations in Zone III to the point where depressed abundances occurred throughout the year. However, our results do not address the question of why substantially lower, and indistinguishable, densities of these amphipods are found in bathymetric Zones I and II.

The presence of dissolved sulfides in marine or estuarine sediments generally is attributed to the incorporation of relatively high amounts of organic material, and its subsequent

consumption by aerobic bacteria that depletes the pore water's oxygen concentration. Anaerobic bacteria then continue to break down the residual organic material, utilizing sulfate provided by the overlying marine water as the terminal electron acceptor and producing dissolved sulfides (Theede et al., 1969; Wang and Chapman, 1999). As described above, the accumulation of benthic algae in marine and estuarine ecosystems often leads to such chemically reduced conditions in the surficial sediment. Thus, for each of the three bathymetric zones within the two band transects, we obtained average densities of benthic green macroalgal (BGM) biomass between Winter 2000 and Winter 2001 for each survey (Figure 6). (Red and brown macroalgae were found to account for less than 1 % of these totals.) These results indicate that a large majority of the accumulated macroalgae occurred between June and November 2000. Therefore, we obtained overall mean ( $\pm$  std. err.) and median values for accumulated BGM densities during this time interval for the three bathymetric zones of each site (Table 9). This summary shows that, during this growing season, more BGM accumulated on the sediments of the Idaho Pt. transect. Ratios of the overall mean densities of BGM at this site and at the Coquille Pt. site were 1.22, 1.26, and 1.88, for Zones I, II, and III, respectively. (Corresponding ratios of the median values are 1.19, 1.22 and 2.70). However, application of the Welch two-sample t-test for non-equal variances to the underlying survey means for these zones showed that only the difference between the site seasonal means for Zone III was statistically significant ( $p < 0.05$ ). The very large differences in pore water concentrations of  $\Sigma S^-$  at the two sites between September and December 2000 (Table 7) are much greater than the differences in the June - November average or median benthic macroalgae accumulation (approximate factors of 2 and 3, respectively). However, the results of the surficial sediment TOC analyses between June and October/November (Figure 4) do indicate distinctly higher concentrations at the Idaho Pt.

transect between July and September, but only at the lowest four station lines (A – D) within, or just upslope of, the intertidal eelgrass meadow. One possible explanation is that the differences in TOC values resulted from the earlier seasonal accumulation of BGM biomass off Idaho Pt. (Figures 2 and 6). Average ( $n = 6$ ) biomass values ( $\pm$  std. err.) for Zone I on June 1-2 were  $114 \pm 44$  and  $8 \pm 3$  g dw/m<sup>2</sup> at the Idaho Pt. and Coquille Pt. transects, respectively. (Corresponding values for native eelgrass above-ground biomass were  $44 \pm 15$  and  $56 \pm 14$  g dw/m<sup>2</sup>, respectively.) The results of the grain size distribution measurements made on the July survey samples (Figure 5) did indicate higher percentages of fine-grain sediment (silt and clay) within Zones I and II. Thus, one hypothesis for the higher  $\Sigma S^-$  concentrations found along the Idaho Pt. transect is that the differences for Zones I and II resulted from the finer sediments in these zones off Idaho Pt., whose lower porosity might have reduced the rate of oxygen diffusion from the sediment interface. The corresponding hypothesis for the differences in  $\Sigma S^-$  concentrations between sites for Zone III is that this resulted from the 2-fold to 3-fold higher levels of accumulated BGM at Idaho Pt. (Table 9). However, resolution of these issues will require additional investigation.

## SUMMARY

This study documented distinct differences in pore water concentrations of total dissolved sulfides ( $\Sigma S^-$ ) in surficial sediments (0-5 cm) from the Idaho Pt. and Coquille Pt. band transects in Yaquina Bay, Oregon. Over a two-week period in summer 2000, concentrations off the former site increased approximately 100-fold, and during the next three months peaked at 2300  $\mu M$ , while the highest concentration measured along the Coquille Pt. transect across the channel was about 8  $\mu M$ . The highest survey median value for the latter site was 0.05  $\mu M$ , while median

concentrations obtained for the four surveys conducted during September - November at the Idaho Pt. site were 57, 84, 75, and 85  $\mu\text{M}$ .

Distinct differences in distributions of infaunal invertebrates between the two sites also were observed. For a bathymetric interval (Zone III) that included approximately 70% of the area of each of the intertidal band transects, between June and December the Idaho Pt. zone had a substantially lower abundance of benthic amphipods than did that off Coquille Pt. The median ratio for the densities of amphipods within Zone III at these two sites was 0.034, corresponding to a median reduction factor of 97% for total amphipod density at Idaho Pt. relative to the Coquille Pt. reference site. Substantially lower burrow densities of benthic shrimp along the Idaho Pt. transect also were observed between July and September within Zone III, and at the three bathymetric line stations just upslope of the native eelgrass upper boundary (Zone II). In September 2000, the month of maximum  $\Sigma\text{S}^-$  concentrations, shells of infaunal bivalve mollusks were observed on the sediment surface within the 0.25  $\text{m}^2$  survey quadrats at 14 of the 16 sulfide stations (including Zone I within the eelgrass meadow) off Idaho Pt. but only at one station off Coquille Pt. Application of measured pore water pH, salinity and sediment temperature values to the measured  $\Sigma\text{S}^-$  concentrations yielded median values for un-ionized  $\text{H}_2\text{S}$  concentrations of 21 to 44  $\mu\text{M}$  for the September to November survey interval. In comparison, calculation of the concentrations of un-ionized  $\text{H}_2\text{S}$  corresponding to the  $\text{LC}_{50}$  values for  $\Sigma\text{S}^-$  reported from laboratory toxicity tests yielded an overall median value of about 5.5  $\mu\text{M}$   $\text{H}_2\text{S}$  for marine infaunal or epibenthic crustaceans and bivalve mollusks. Thus, it appears that the  $\Sigma\text{S}^-$  concentrations measured in surficial sediment samples from the Idaho Pt. transect during summer and fall 2000 were high enough to have caused the differences in distributions of infaunal invertebrates observed between the two study sites.

Relatively high average values were obtained for the biomass of benthic green macroalgae for bathymetric zones I, II, and III of the Idaho Point transect. Peak survey averages for these zones were approximately 300, 500, and 300 g dw/m<sup>2</sup>, respectively. These values are comparable to those found in the literature cited above to be associated with depressed abundances, or altered behavior, of benthic infaunal invertebrates, principally amphipods and bivalve mollusks. The average (or median) density of benthic macroalgae in Zone III of the Idaho Pt. transect between June and November 2000 was approximately two to three times that obtained in this zone off Coquille Pt.; this difference may have contributed to the major differences in  $\Sigma S^{--}$  concentrations and amphipod abundances measured in this zone. Although the corresponding macroalgal densities in Zones II and I off Idaho Pt. exceeded those off Coquille by only about 20–25%, the abundance of fine-grain sediment (< 0.063 mm) at the former site was approximately twice that at the latter site. Thus the finer grain sediment there, with a substantially lower porosity, may have inhibited the transport of oxygenated water from the sediment surface, thus facilitating the buildup of dissolved sulfides in these bathymetric zones.

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## LITERATURE CITED

Buchanan, J.B. 1984. Sediment analysis. In N.A.Holme and A.D. McIntyre (eds.), *Methods for the Study of Marine Benthos, IBP Handbook No. 16, 2<sup>nd</sup> edition*, pp. 41-65. Blackwell Scientific Publications, Oxford, U.K.

Caldwell, R.S. 1975. Hydrogen sulfide effects on selected larval and adult marine invertebrates. Water Resources Research Institute, Oregon State University, Corvallis, OR, USA.

Chapman, J. W. 2007. Amphipoda. In J. T. Carlton (ed.) *The Light and Smith Manual: Intertidal Invertebrates from Central California to Oregon, 4<sup>th</sup> edition*, pp. 545-618. University of California Press, Berkeley.

Cummins, S.P., D.E. Roberts and K.D. Zimmerman. 2004. Effects of the green macroalga *Enteromorpha intestinalis* on macrobenthic and seagrass assemblages in a shallow coastal estuary. *Marine Ecology Progress Series* **266**:77-87.

Gopakumar, G. and V.J. Kuttyamma. 1996. Effect of hydrogen sulphide on two species of penaeid prawns *Penaeus indicus* (H. Milne Edwards) and *Metapenaeus dobsoni* (Miers).

*Bulletin of Environmental Contamination and Toxicology* **57**:824-828.

Hagerman, L. and B. Vismann. 1995. Anaerobic metabolism in the shrimp *Crangon crangon* exposed to hypoxia, anoxia and hydrogen sulfide. *Marine Biology* **123**:235-240.

Hemminga, M.A. and C.M. Duarte. 2000. *Seagrass Ecology*. Cambridge University Press, Cambridge, U.K. 298 p.

Hull, S.C. 1987. Macroalgal mats and species abundance: a field experiment. *Estuarine, Coastal and Shelf Science* **25**:519-532.

DRAFT

Jones, M. and E. Pinn. 2006. The impact of a macroalgal mat on benthic biodiversity in Poole Harbour. *Marine Pollution Bulletin* **53**:63-71.

Knezovich, J.P., D.J. Steichen, J.A. Jelinski and S.L. Anderson. 1996. Sulfide tolerance of four marine species used to evaluate sediment and pore-water toxicity. *Bulletin of Environmental Contamination and Toxicology* **57**:450-457.

Laudien, J., D. Schiedek, T. Brey, H.-O. Portner and W.E. Arntz. 2002. Survivorship of juvenile surf clams *Donax serra* (Bivalvia, Donacidae) exposed to severe hypoxia and hydrogen sulphide. *Journal of Experimental Marine Biology and Ecology* **271**:9-23.

Lewis, L.J., J. Davenport and T.C. Kelly. 2003. Responses of benthic invertebrates and their avian predators to the experimental removal of macroalgal mats. *Journal of the Marine Biological Association of the United Kingdom* **83**:31-36.

Nicholls, D.J., C.R. Tubbs and F.N. Haynes. 1981. The effect of green algal mats on intertidal macrobenthic communities. *Kiefer Meerestorsch Sonderh* **5**:551-520.

Norkko, A. 1998. The impact of loose-lying algal mats and predation by the brown shrimp *Crangon crangon* (L.) on infaunal prey dispersal and survival. *Journal of Experimental Marine Biology and Ecology* **221**:99-116.

Norkko, A. and E. Bonsdorff. 1996. Rapid zoobenthic community responses to accumulations of drifting algae. *Marine Ecology Progress Series* **131**:143-157.

Norkko, J., E. Bonsdorff and A. Norkko. 2000. Drifting algal mats as an alternative habitat for benthic invertebrates: species specific responses to a transient resource. *Journal of Experimental Marine Biology and Ecology* **248**:79-104.

Orth, R.J., T.J.B. Carruthers, W.C. Dennison, C.M. Duarte, J.W. Fourqurean, K.L. Heck, Jr., A.R. Hughes, G.A. Kendrick, W.J. Kenworthy, S. Olyarnik, F.T. Short, M. Waycott and S.L. Williams. 2006. A global crisis for seagrass ecosystems. *Bioscience* **56**:987-996.

Osterling, M. and L. Pihl. 2001. Effects of filamentous green algal mats on benthic macrofaunal functional feeding groups. *Journal of Experimental Marine Biology and Ecology* **263**:159-183.

Raffaelli, D., J. Limia, S. Hull and S. Pont. 1991. Interactions between amphipod *Corophium volutator* and macroalgal mats on estuarine mudflats. *Journal of the Marine Biological Association of the United Kingdom* **71**:899-908.

Sandberg-Kilpi, E., B. Vismann and L. Hagerman. 1999. Tolerance of the Baltic amphipod *Monoporeia affinis* to hypoxic, anoxia and hydrogen sulfide. *Ophelia* **50**:61-68.

Short, F.T. and S. Wyllie-Echeverria. 1996. Natural and human-induced disturbance of seagrasses. *Environmental Conservation* **23**:17-27.

Standard Methods. 1995. Methods 4500-S2 D&F. Methylene blue method and iodometric method. In (A.D. Eaton, L.S. Clesceri and A.E. Greenberg, eds.) *Standard Methods for the Examination of Water and Wastewater*, pp. 4-122 to 4-131. American Public Health Association, 1015 Fifteenth St., NW, Washington, DC.

Tetra Tech. 1986. Recommended protocols for measuring conventional environmental variables in Puget Sound. Final Report TC-3991-02. Prepared for the U.S. Environmental Protection Agency. Tetra Tech, Inc. 11820 Northrup Way, Bellevue, Washington.

Theede, H., A. Ponat, K. Hiroki and C. Schlieper. 1969. Studies on the resistance of marine bottom invertebrates to oxygen-deficiency and hydrogen sulfide. *Marine Biology* **2**:325-337.

Theede, H. 1973. Comparative studies on the influence of oxygen deficiency and hydrogen sulfide on marine bottom invertebrates. *Netherlands Journal of Sea Research* **7**:244-252.

Tubbs, C.R. and J.M. Tubbs. 1983. Macroalgal mats in Langstone Harbour, Hampshire, England. *Marine Pollution Bulletin* **14**:148-149.

Wang, F. and Chapman, P.M. 1999. Biological implications of sulfide in sediment - A review focusing on sediment toxicity. *Environmental. Toxicology and Chemistry* **18**: 2526-2532.

Young, D.R., D.T. Specht, B.D. Robbins and P.J. Clinton. 1999. Delineation of Pacific Northwest SAVs from aerial photography: natural color or colour infrared film? In: *Proceedings of the 1999 American Society of Photogrammetry and Remote Sensing Annual Conference*, pp. 1173-1178. American Society of Photogrammetry and Remote Sensing, May 17-21, 1999, Bethesda, MD.

Young, D.R., R.J. Ozretich, D.T. Specht, J.O. Lamberson, R.S. Caldwell, G.I. Hansen, B. Stoffey and P. Clinton. 2003. Relationships between water and sediment characteristics and benthic green macroalgal abundance in Yaquina Bay, Oregon: 1999-2000. Presented at the Meeting of the Phycological Society of America, Gleneden Beach, OR, June 14-19, 2003.